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HOUSEHOLD PORCELAIN WITH MINERALIZING ADDITIVES

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The effect of mineralizing agents on the structure and properties of porcelain based on raw materials from Bulgaria is considered. The optimum limits for additives and the processes occurring in firing of materials are identified. The articles obtained in accordance with the developed technology in certain parameters surpass the current standard requirements.

To ensure the competitiveness of household porcelain, manufacturers use high-quality materials containing a limited amount of chromophore impurities.

Various compositions for porcelain mixtures were proposed based on sands and quartz-feldspar rocks from Bulgaria, as well as bentonite. In this context, the authors investigated the effect of mineralizing additives on the sintering, structure, and properties of porcelain based on Bulgarian raw materials.

The experimental mixtures included three types of kaolin, whose content was approximately 50% (here and elsewhere weight content is indicated), and also bentonite, sand, and pegmatite. The reference composition was the porcelain mixture used at the Kitka factory, which is based on the quartz sand from the Kaolinovo deposit (Bulgaria).

The experimental mixtures were prepared according to the traditional technology; the samples were fired in a tunnel furnace and in a fast-firing furnace up to a temperature of $1350 \pm 10°C$, under the conditions used in household porcelain production. The estimated chemical compositions of the experimental and the standard porcelain mixtures were virtually identical. However, the experimental mixtures had a slightly lower level of plasticity than the industrial mixture, although its variation limits were quite acceptable for the production process.

A specific feature of the structure of the experimental mixtures based on Bulgarian materials is their substantial content of cristobalite, which is present together with mullite crystals, quartz grains, and the vitreous phase. Certain quartz grains were completely fused and formed areas of high-silicon glass.

The quantitative x-ray phase analysis established that the experimental materials are characterized by an increased content of mullite, quartz, and cristobalite, compared to the content of these components in the phase composition of the industrial porcelain. This can be accounted for by the simultaneous use of quartz sand and high-quality bentonite, which was one of the conditions for the formation of what is known as cristobalite porcelain. The maximum quantity of cristobalite was registered in experimental porcelain (16%), and its content in the initial porcelain was only 3%. The effect of complex additives on the structure and properties of porcelain was studied with the aim of controlled improvement of consumer properties of porcelain, in particular, its whiteness.

A complex additive containing zinc and magnesium oxides was introduced into experimental mixtures. The total zinc oxide content did not exceed 1%, and that of magnesium carbonate 2%. The composition and the quantity of the additive were selected based on the analysis of published data, as well as preliminary experimental results. The ratio between zinc oxide and magnesium oxide in the complex additive varied from 1 : 3 to 1 : 1.

As a result of studying the physicochemical processes occurring in sintering, it was found that the temperature intervals of the endothermic effect in experimental porcelain mixtures with additives are close to the analogous temperature intervals in the initial mixture. As the ratio of zinc oxide to magnesium oxide in the additive increases, the starting temperature of the endothermic effect decreases by 20 – 25°C, and the interval of this effect remains within the limits of 165 to 200°C. The minimum temperature of the endothermic effect in experimental mixtures with a complex additive is registered virtually at the same temperature as in the initial mixture. It can be supposed that at these temperatures the effect of the additives is not yet manifested.

The temperature interval of the exothermic effect in experimental mixtures with a complex additive shifts to a lower temperature region, compared to the initial mixture. Accordingly, the sintering of mixtures with additives starts at a lower temperature than the sintering of the initial mixtures,

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namely, around 1220°C. Such a decrease in the temperature can be attributed to the effect of the additive on an earlier formation of aluminosilicate melt of decreased viscosity, which improves the diffusion processes and is accompanied by the consolidation of the material at lower temperatures. These processes contribute to increasing deformation, recrystallization of primary mullite to secondary mullite, and conversion of α-quartz to cristobalite, which modifies the porcelain structure.

It is also established that the introduction of the complex additive consisting of zinc and magnesium oxide to the porcelain mixture is accompanied by a decrease in the temperature of firing porcelain materials. Stable compaction of materials with additives begins already at 1250°C, and at the optimum firing temperature equal to 1320°C their apparent density is within the limits of 2.40 – 2.42 g/cm^3. The experimental materials in this parameter satisfy the requirements imposed on hard porcelain, which makes it possible to recommend them for the production of articles with increased mechanical strength.

The structure of experimental materials is heterogeneous and consists of mullite, quartz, cristobalite, and feldspar pseudomorphosis.

The introduction of the complex additive in experimental porcelain mixtures intensifies the formation of mullite, whose amount grows from 22% in the initial material to 27% in the optimum composition of the experimental material. The mullite content in all experimental mixtures amounted to 25 – 27%, which exceeded by 3 – 5% the content of mullite in the initial porcelain.

The structure of materials exhibits a decrease in the quartz content from 21 to 14%, and the quartz content in the experimental materials is within the limits of 14 – 16%.

A significant distinction in the phase composition of material with additive from the initial material consists of the almost double content of cristobalite (increased from 8 to 17%). The cristobalite content in the experimental material varied from 13 to 17%.

It was also found that the vitreous-phase content decreased by 10% compared to the initial material. This suggests that the physicotechnical properties of porcelain with additives are better, in particular, its mechanical strength and whiteness.

Furthermore, an increasing content of additives developed the conditions for intensifying the crystal-phase formation. This was reflected in the increased overall quantity of the crystal phase and in the increased degree of homogeneity of the vitreous phase due to merging of its separate extremely small sites with the formation of local vitreous sites, whose size reached 1 μm. The study also registered the complete fusion of isolated vitreous sites into larger areas, in which mullite crystals of size 0.2 μm were uniformly distributed. This process is accompanied by a decrease in the phase boundaries, which can also have a positive effect on increasing the porcelain whiteness.

The analysis of the properties of porcelain mixtures and experimental materials established that the introduction of complex additives increases the plasticity number from 26.6 to 34.3, enhances the total shrinkage from 14.4 to 17.2%, and nearly doubles the deformation level.

The mechanical strength of materials with additives fired at temperatures 1300 and 1350°C exceeded the strength of the initial material by approximately 14.5% and reached 92 – 99 MPa. The thermal resistance of experimental materials made of porcelain mixtures with additives and decorated with industrially produced glaze was the same as in industrial porcelain and amounted to about 200°C, which satisfies the current standard requirements.

The introduction of the complex additive into experimental mixtures had a positive effect on the whiteness and translucence of the porcelain. Thus, the whiteness of the porcelain with the additive of the optimum composition increased by 6 – 7%, which is due to the modified microstructure of the experimental material. The electron microscope and x-ray phase analysis of experimental ceramic materials established that the porcelain with the additive of the optimum composition has a more homogeneous structure compared to the industrial porcelain structure, a higher degree of mullitization, and an increased content of mullite, which forms a dense lattice of needle-shaped and acicular crystals.

It can be supposed that under the effect of the additive the mullitizing degree of the main porcelain mixture increases, its viscosity decreases, and the activity of aluminosilicate glass-forming melt becomes higher, which improves the growth, shape, and distribution of mullite crystals. These factors have a significant effect on increasing the mechanical strength and whiteness of porcelain.

The porcelain mixture with additives was used in industrial conditions to make articles whose parameters of water absorption, deformation, translucence, mechanical strength, and thermal resistance surpassed the current standard requirements. Furthermore, the 6% increase in the whiteness of porcelain materials contributes to increasing the competitiveness of the product.